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**DETERIORATION OF CALCIUM-STABILIZED ZIRCONIA AS THE RESULT OF
THERMAL CYCLING**

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INTRODUCTION

Zirconia is considered to be an outstanding refractory material because of its ability to withstand temperatures above 4000°F. However, the use of zirconia is limited because of its susceptibility to failure from thermal shock. The poor thermal shock resistance of zirconia is caused by a crystalline inversion which occurs at 1830°F (fig. 1) with an accompanying destructive change in volume. Additions of calcium oxide have been found to produce a new crystal structure which eliminates crystalline inversions. Increased amounts of calcium oxide added to zirconia increase the degree of stabilization and overall thermal expansion (fig. 1). An addition of four to five weight percent of calcium oxide produces a partially stabilized material whose major crystalline component is cubic zirconia with a significant amount of monoclinic zirconia. The latter is present to reduce the overall thermal expansion for thermal-shock resistance. The improvement of the zirconia properties achieved through partial stabilization with lime apparently is not sufficient to permit its use for extended periods of time in applications producing thermal cyclic conditions. One such application is a heat exchanger as used in the 11 inch ceramic-heated jet blowdown tunnel at Langley Research Center, Virginia.

The zirconia refractories in the heat exchanger are bricks, used as the innermost lining of a high pressure, high temperature vessel, and pebbles, used as the heat-exchanging element within the vessel. The function of the tunnel is to test the effects of high temperature, pressure, and velocity on materials considered for use in constructing missiles and satellites. The procedure used in producing optimum conditions is to heat the top or the pebble bed in excess of 4000°F., to pressurize the vessel to its maximum pressure capability, and finally to force ambient air through the hot pebble bed and out of the vessel through a small orifice into a contoured test chamber. A single cycle or test

of heat up and blow down. It takes approximately three hours to heat the pebble bed to 4000°F from an idling temperature of 2500°F . The pebble bed is heated from the top (fig. 2), therefore, the region directly exposed to the burner flame realizes the 4000°F temperature while the remainder of the vertical column of pebbles and liner shows a temperature gradient dependent on the thermal conductivity of the zirconia during the heating-up portion of a blow-down cycle. Two or three blow-down operations are possible in one day. The blow-down portion of the cycle takes approximately four minutes with a pebble bed drop from 4100°F to 3600°F . The thermal shock produced by the cyclic reaction results in spalling and deterioration or physical breakdown of the brick and pebbles. Spalling is a normal result of thermal shock. Deterioration is a product of time and temperature and is found in localized areas of the zirconia lining and pebble bed where the temperature cycles in a range from 1600°F to 2000°F (fig.3).

The object of this investigation was to study the physical changes in stabilized zirconia caused by thermal cycling and the relationship of these changes on the loss in strength of refractory shapes that have been cycled into the critical temperature range.

REVIEW OF LITERATURE

The use of zirconia as a high temperature refractory was recognized as early as 1900. This material was found to have: (1) good resistance to transfer of heat, (2) inertness to most chemicals, (3) stability in oxidizing atmospheres, and (4) good load-bearing strength at temperatures in excess of 4000°F . The primary problem encountered in using zirconia is the inversion and accompanying drastic volume change experienced on heating or cooling the material to 1830°F .

The process of eliminating or limiting inversion is called stabilization. The use of stabilized zirconia on a commercial basis was started in 1947⁽²⁾. Numerous materials have been successfully used in stabilizing zirconia either partially or completely. Combinations of calcium oxide and magnesium oxide were found to be very good stabilizers; however, calcium oxide proved to be the best and most

economical stabilizer⁽³⁾. Curtis stated that, "A small amount of inversion may be necessary for high resistance to thermal shock in zirconia ware because: (1) the overall thermal expansion is then small and gradual, and (2) with complete elimination of inversion the expansion is large since the expansion curve is a straight line and the coefficient of expansion is high" (fig. 1). The best thermal shock resistance was obtained by additions of four weight percent of calcium oxide to zirconia (3). Duwez and Odell in a study of zirconia stabilization found that compositions containing less than eight weight percent of calcium oxide had varying degrees of inversion increasing as the calcium oxide content decreased. Compositions between eight weight percent and 16 weight percent contained only cubic zirconia as the result of the formation of an interstitial solid solution of calcium oxide in zirconia with no inversion present. Zirconia with more than 16 weight percent of calcium oxide contained a calcium oxide-zirconia solid solution and calcium zirconate (4). The effect of reheating partially and fully stabilized zirconia at critical temperatures for long periods of time indicated that no significant change in structure occurred as a result of isothermal treatments. Isothermal treatment consisted of reheating zirconia samples with varying degrees of stabilization to 1375°C for 336 hours, 1200°C for 540 hours, 1100°C for 812 hours, 980°C for 1473 hours, and 815°C for 2011 hours⁽⁴⁾. Weber, Garrett, Mauer, and Swartz substantiated Duwez and Odell's work on the stability of the calcium oxide-zirconia solid solution when isothermally heat treated. They further showed that a magnesium oxide-zirconia solid solution was not phase stable and became unstabilized when isothermally treated at temperatures between 815°C and 1375°C⁽⁵⁾.

The structure of zirconia in varying degrees of stabilization has been studied by means of X-ray diffraction. Three diffraction peaks have been used to identify the phase present and to calculate the percent of zirconia stabilization quantitatively⁽⁶⁾ (fig. 4).

PROCEDURE

The material used in this investigation was fused, stabilized zirconia produced by the Norton Company having a composition of 4.05 percent CaO , 0.95 percent SiO_2 , 0.18 percent Fe_2O_3 , 0.27 percent TiO_2 , and 94.50 percent ZrO_2 . The Ballard and Marshall process of manufacturing stabilized zirconia directly from ores was used to produce the material. (2)

During a periodic maintenance and rebricking operation of the blow-down tunnel at Langley Research Center, it was observed that there were sections within the furnace wall and in the pebble bed that were very weak and friable. This deteriorated zone is shown in figure three. Twenty thermocouples were placed throughout the brickwork in the rebuilt furnace so that temperature in the wall could be recorded during normal operation of the furnace. It was subsequently determined that the temperature in the zone of refractories that were deteriorating cycled between 1600°F and 2000°F . As would be expected from the description of the furnace operation as previously given, this zone varied in its location with respect to the inside of the furnace wall because of the temperature gradient from top to bottom in the furnace.

Simulation of the temperature cycling experienced by the refractories in the furnace was accomplished by placing one-inch cubes of zirconia cut from an unused brick along with three-eighth-inch diameter pebbles in a laboratory kiln. The kiln was cycled between 1000°F and 2100°F at a heating rate of 12.5°F per minute and a cooling rate of 5°F per minute. It was felt that this cooling and heating schedule would not be rapid enough to cause thermal shock damage due to large temperature gradients.

Friable material taken from the critical-temperature zones in the heat exchanger and samples from the laboratory tests were compared with unused zirconia refractories. The crystal structure and calcium oxide content of the samples were determined by x-ray diffraction and spectroscopic procedures. The ratio of the amount of cubic phase zirconia to monoclinic phase is reported as the degree of stabilization. The Norton

Company supplied a graph (see Figure five) showing the relationship between the degree of stabilization and the ratio of the intensities of the cubic and monoclinic diffraction peaks. Peaks at $28^{\circ}20$ and $30^{\circ}20$ were used (fig.4).

In order to determine whether or not the calcium oxide present in the zirconia samples was combined in solid solution or occurred as free lime, samples were leached in diluted hydrochloric acid (50 percent concentrated acid, 50 percent water), and the calcium oxide content after leaching was compared to the lime content of the same sample before leaching. (Fig 6)

Brick from the heat-exchange furnace were sectioned as shown in figures 7-A and 7-B. Because of the temperature gradient through the furnace wall, the sections had experienced cycling through different temperature ranges, and each section was checked for the crystal phases present and calcium oxide content.

Deteriorated brick were reheated to 3000°F . for two hours and analyzed by X-ray diffraction.

RESULTS AND DISCUSSION

As previously stated, information obtained from thermocouples placed in the heat-exchange furnace showed maximum deterioration of the refractories in those zones in which the temperature varied from 1600°F to 2000°F . Similar results were obtained in the laboratory cycling tests. The one-inch-cube specimens collapsed when touched after being cycled 41 times between 1100°F and 2100°F .

A used, deteriorated brick was crushed simply by rubbing it by hand and then separated into several grain sizes. The results of tests run on these sizes as compared to an unused refractory are shown in Table I. It can be seen that the cubic zirconia is concentrated in the coarse sizes, and the lime, although present in the -325 mesh material, is no longer in solid solution but is found as free lime (as is shown by acid leaching). The fact that the monoclinic phase is found in the fine fractions indicate that the inversion from monoclinic to tetragonal zirconia during cycling resulted in a grinding action to reduce the grains to smaller sizes. Also, the amount of calcium oxide in solid solution with zirconia in the unused refractory is only three weight percent. The CaO-ZrO_2 phase diagram(4) shows that more lime is necessary

than this amount to produce a zirconia consisting of 80 percent cubic phase and 20 percent monoclinic phase.

Analyses of two bricks are given in Tables II and III. These refractories were taken from the wall of the blow-down tunnel after the tunnel had been in operation for some time. The piece used to obtain the data shown in Table II was exposed on one face to a maximum temperature of about 4000°F. During the time when the furnace was idling, this face was held at 2300°F. The temperature of the cold face of the refractory was from 1600° to 2100° F. during furnace operation and 1300°F during idling. Maximum physical deterioration of the piece occurred at the cold face. Although the hot face was not subjected to a temperature below 2300°F, those sections behind the hot face (sections two through six) were subjected to lower temperatures. Maximum destabilization of the refractory is seen to have occurred in that portion of the piece that was subjected to cyclic temperature changes in the range of 1600° to 2100°F. Similar results were obtained on a brick that was taken from a cooler position in the furnace (Table III). These results show destabilization to occur in the temperature range in which crystalline inversions take place. During heating and cooling between approximately 1500° and 2100°F. there is a reversible change from monoclinic to tetragonal zirconia accompanied by an increase or decrease in the amount of cubic phase present ⁽⁴⁾. As can be seen from figure I these inversions take place with a considerable volume change.

Destabilized, deteriorated brick that were reheated to 3000°F. for two hours were changed to their original condition - 80 percent stabilized - and regained their strength. The fact that most of the lime is uncombined with zirconia in deteriorated material, as is shown by the acid-leaching tests, indicates diffusion of the calcium from the cubic phase at relatively low temperatures. The work of Duwez, Orell and Brown showed that there was no migration of lime from solid solution over extended time periods of isothermal heat treatment and thus no destabilization of the material. This investigation has shown that cyclic heat treatment in the temperature range at which crystalline inversions occur will result in lime migration and destabilization.

Destabilization is the result of diffusion of the calcium oxide out of solid solution during cyclic temperature changes. The lime strains the zirconia lattice in forming a cubic phase because of the large difference in ionic sizes of calcium and zirconium. At high temperatures, the expanded cubic lattice is able to accommodate the calcium ion, but at lower temperatures more strain is imposed on the lattice and the tendency for calcium to be expelled from the lattice increases. However, the energy available for diffusion decreases as the temperature decreases. Therefore, as the temperature is lowered there are two opposing forces working - one favoring destabilization and one favoring retention of the cubic phase.

Maximum destabilization occurs, however, in the temperature range in which monoclinic zirconia inverts to tetragonal zirconia. This suggests that the presence of unstabilized zirconia affects the destabilization of cubic material. A large volume change accompanies the monoclinic to tetragonal inversion. This expansion on cooling would cause mechanical strains to be imposed on adjacent grains of cubic zirconia, and compressive strains would favor the migration of calcium out of the cubic lattice.

To test this hypothesis, two stabilized zirconia samples were cycled from 1100°F to 2100°F. One sample was 85 percent stabilized (85 percent cubic and 15 percent monoclinic) and the other was 100 percent stabilized. After 47 cycles the partially stabilized material contained only 58 percent cubic zirconia whereas the completely stabilized material still contained 99 percent cubic phase. After 100 cycles the completely stabilized material contained 95 percent cubic zirconia.

It is felt that these results show the destabilizing effect of monoclinic zirconia on cubic zirconia.

CONCLUSIONS

1. The primary reason for mechanical failure of the zirconia refractories was sudden volume changes due to the monoclinic to tetragonal inversion. This condition is brought about by cyclic heating in the 1600°F to 2000°F range.

2. The presence of unstabilized zirconia increases the rate at which calcium oxide is diffused from the cubic lattice when the material is cycled between 1600°F and 2100°F. Such heat treatment will result in destabilization and mechanical deterioration of the refractory.

3. Less calcium oxide is required to produce a zirconia that is 80 percent stabilized than is shown on the CaO-ZrO₂ phase diagram.

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TABLE X.

PROPERTIES OF USED AND UNUSED STABILIZED ZIRCONIA REFRACTORIES

<u>Specimen</u>	<u>Stabilization</u>	<u>Calcium Oxide</u>	<u>Color</u>
Unused	80.0%	4.0% (wt.)	Light Orange or Buff
Unused (Acid Leached)	80.0	3.0	Light Orange or Buff
Used*			
(1) Full Specimen	51.0	5.0	Yellow
(2) Fractionated specimen.			
+80 mesh	81.5	4.1	
-80, +200 mesh	54.0	5.0	
-200, +325 mesh	21.0	5.0	
-325 mesh	<5.0	4.6	
-325 mesh (acid leached)	<5.0	0.5	

*Cycled from 1600° F. to 2000° F. during operation of heat-exchange furnace.

TABLE II.
PROPERTIES OF STABILIZED ZIRCONIA BRICK AFTER USE IN THE
HOT ZONE OF THE CERAMIC HEAT
EXCHANGER

<u>Sectioned Sample</u>	<u>Stabilization</u>	<u>Calcium Oxide,</u>	<u>Color</u>
Section 1, Hot Face Max. Temp. 4000 F., Idle - 2300 F.	81.5%	3.7% (wt.)	White
Section 2	68.5%	3.3%	Whitish-tan
Section 3	63.5%	3.8%	Tan
Section 4	65.0%	3.9%	Tan
Section 5	66.0%	3.9%	Tan
Section 6	53.5%	4.5%	Tan to red Orange
Section 7, Cold Face Max. Temp. 1600 - 2100 F. Idle - 1300 F.	51.0%	5.0%	Tan to red Orange

TABLE III.

PROPERTIES OF STABILIZED ZIRCONIA BRICK AFTER USE IN THE 2000° F.
TO 1600° F ZONE OF THE CERAMIC HEAT EXCHANGER

<u>Sectioned Sample</u>	<u>Stabilization</u>	<u>Calcium Oxide</u>	<u>Color</u>
Section 1, Hot Face (2000° to 1600° F) Idle Temp. 1000° F.	61.5%	3.87% (wt.)	Orange
Section 2	61.5%	4.1%	Orange
Section 3	58.0%	4.1%	Tan
Section 4	66.0%	4.3%	Tan
Section 5	67.5%	4.5%	Light Orange to Buff
Section 6 (600° F) Idle 1600° F High Fire	70.0%	4.1%	Light Orange to Buff

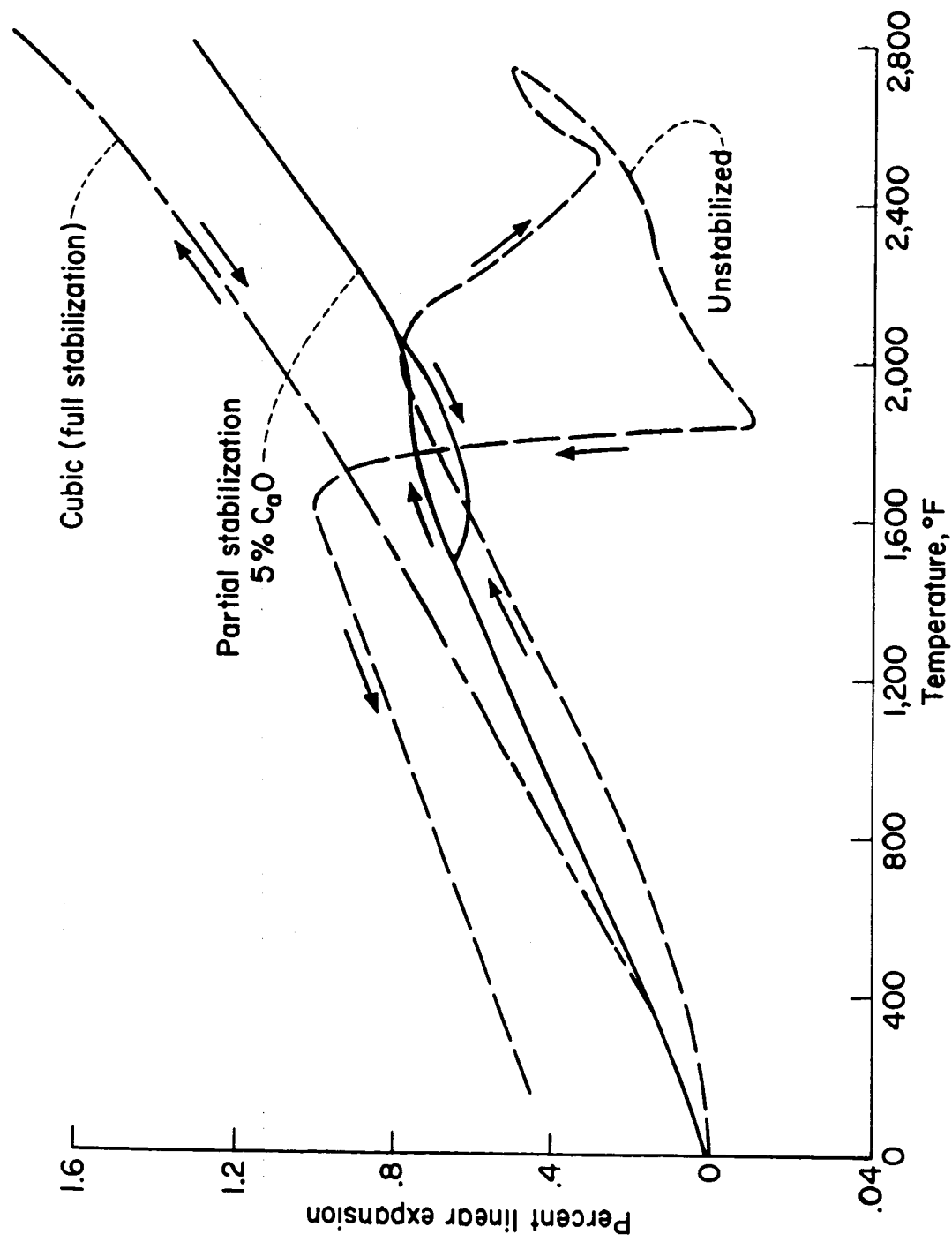


Figure 1.- Thermal expansion of zirconia (1).

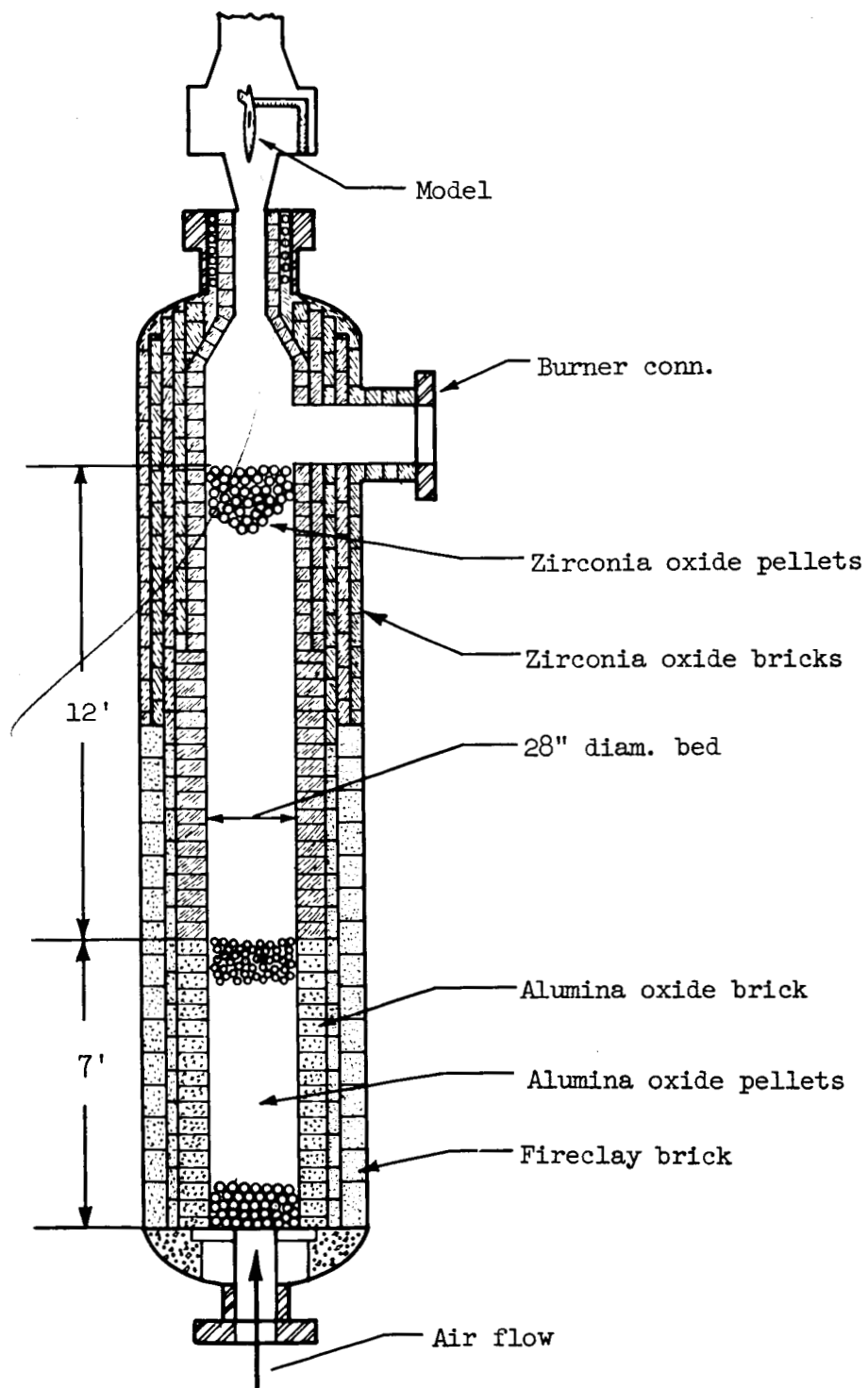


Figure 2.- Pilot model, ceramic heater.

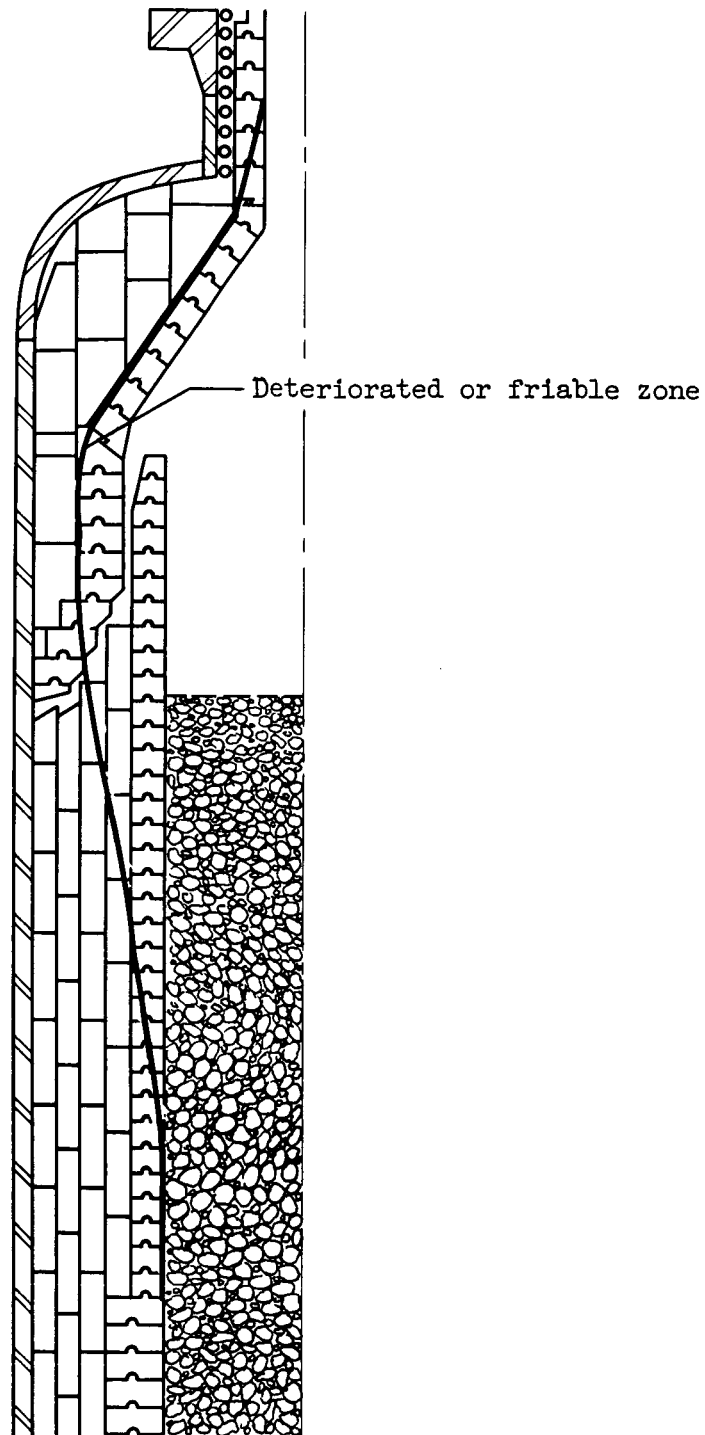


Figure 3.- Section of pilot model, ceramic heater

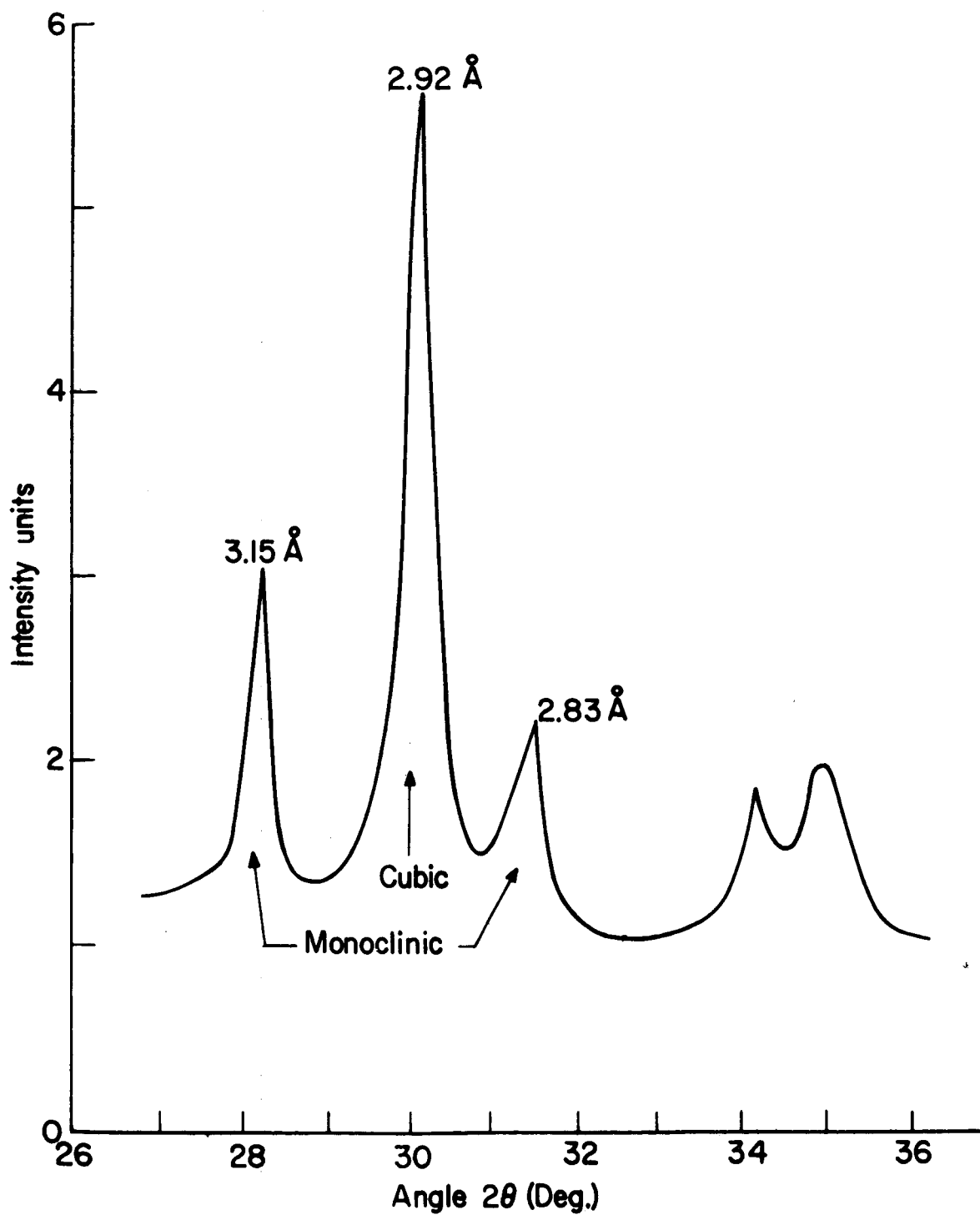


Figure 4.- X-ray diffraction curve for 70 percent cubic - 30 percent monoclinic zirconia⁽²⁾. (CaO:4.5 to 5 Wt percent - Cu K α radiation.)

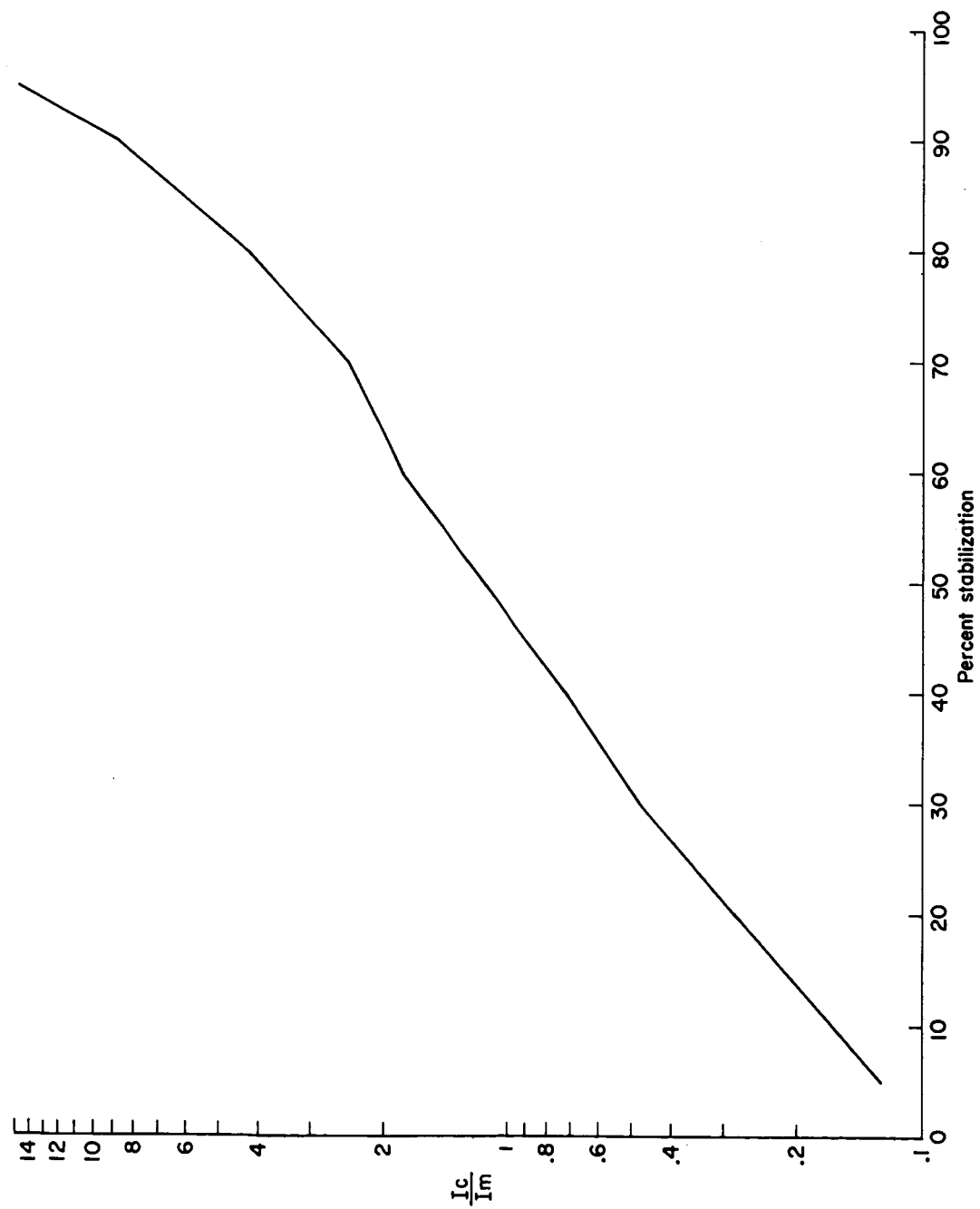


Figure 5.- Stabilization of ZrO_2 .

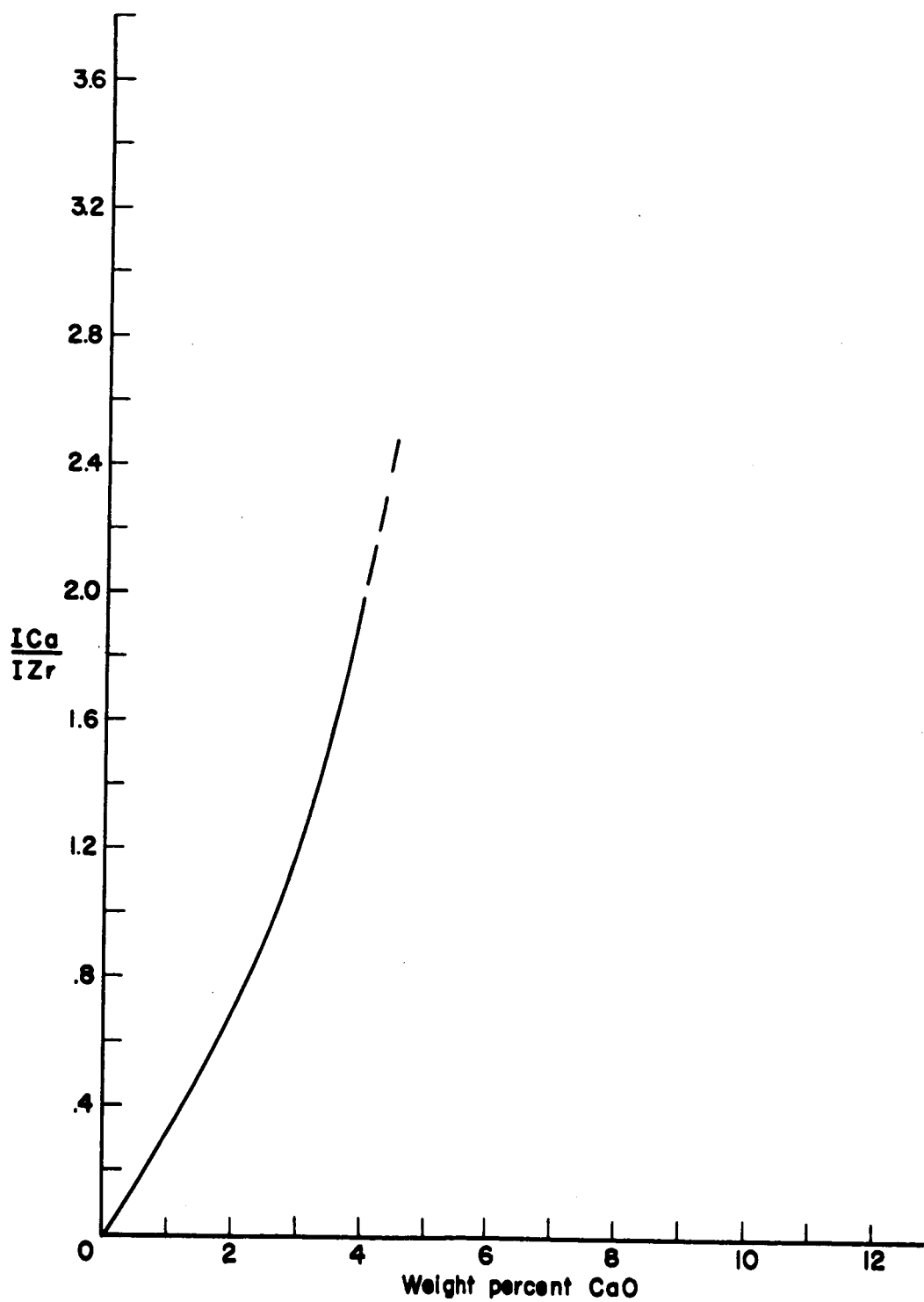


Figure 6.- Calibration curve for CaO analysis.

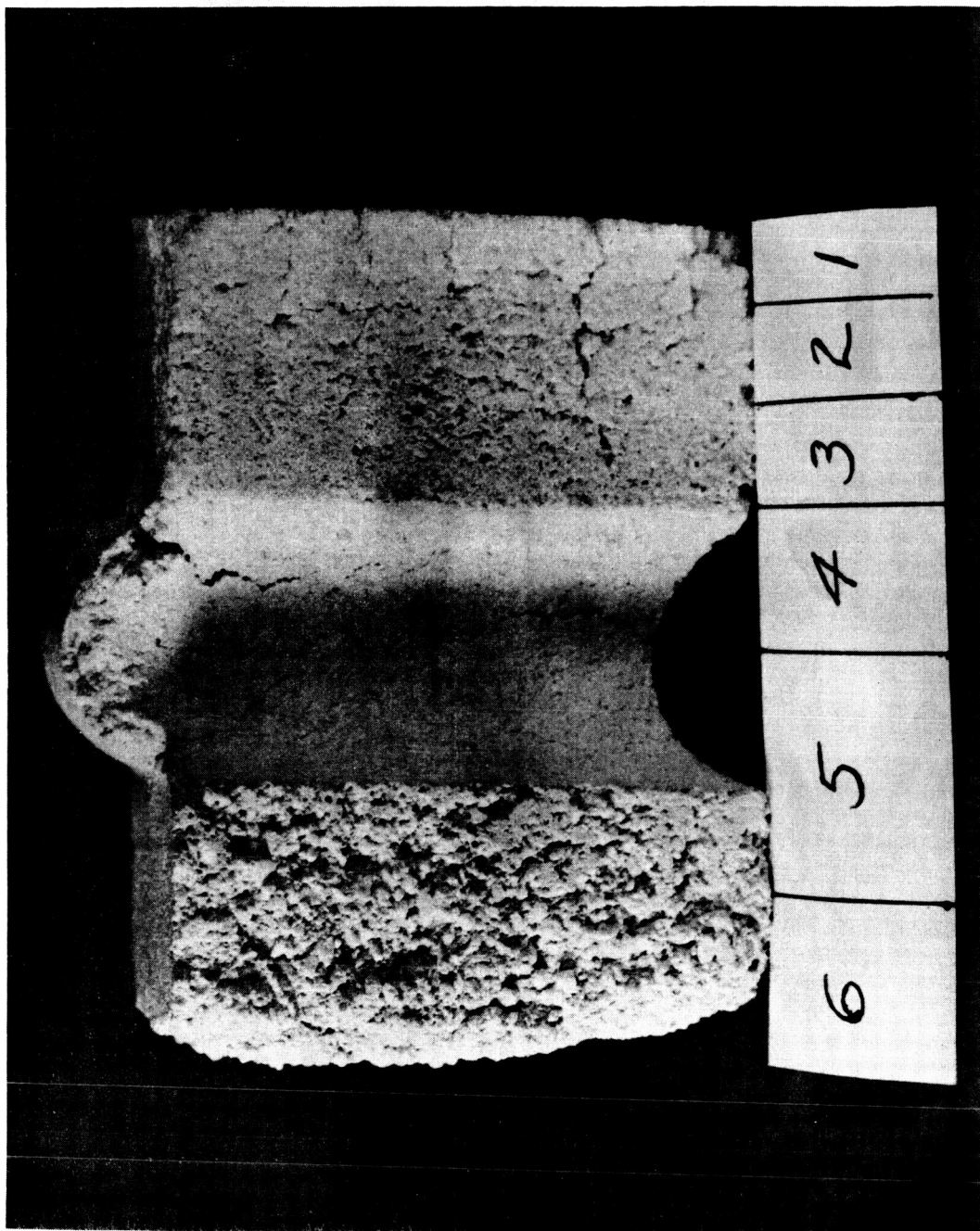


Figure 7(a).- Lime stabilized zirconia brick (used). (1) Hot face and (6) cold face.

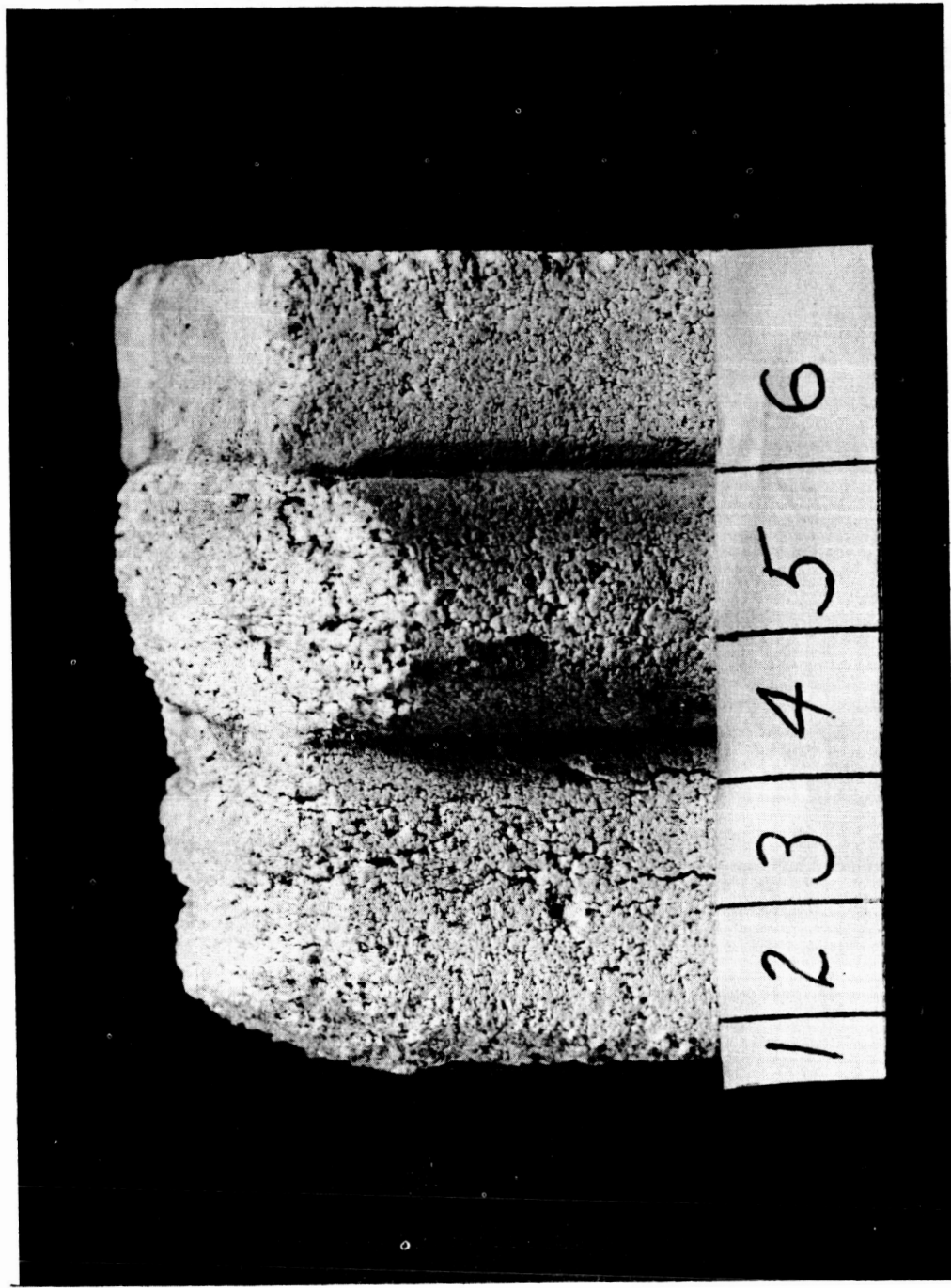


Figure 7(b).-- Lime stabilized zirconia brick (used). (1) Hot face and (6) cold face. I-61-2154